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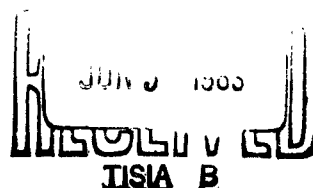
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Thermoelectric Junctioning Project

A B S T R A C T

The effort expended in the second quarter's work on this project was mainly concerned with evaluation of solder alloys and their characteristics. The best solder series discovered during this period was a combination of bismuth, tin and antimony. Workable solders of this series have been developed with melting points ranging from 400°F to 273°F.

Because surface cleanliness and preparation technique are extremely important in producing a superior solder joint, studies involving surface examination through electron microscopy have been initiated to determine the surface contaminants.

The sensitivity of the joint resistance scanner has been improved by one order of magnitude to accurately determine resistance to 1×10^{-7} ohms.

I. INTRODUCTION

The work accomplished during the first quarter of this investigation was intended to determine a method or methods of sample pretreatment to prepare thermoelectric materials for soldering and to determine the flux most effective for the actual soldering operation. Of the various fluxes tested, hydrochloric acid was the only reagent which produced a discernible effect on a prepared sample. It was also apparent that neither of the two material pretreatment methods selected had any measureable effect on improvement of the fluxing action.

Because of the inconclusiveness of the initial flux evaluation it was decided to rerun the flux evaluation in conjunction with a solder analysis which required analysis of the combined effects of flux and solder on a thermoelectric material surface.

Because the methods of pretreatment of the thermoelectric material also did not exhibit any measureable difference, a single method was used for the balance of this portion of the investigation. This method was intended to remove cutting residues and any surface or entrained contaminants.

II. EXPERIMENTAL WORK

A. Solder Analysis

In order to best evaluate the performance of a particular solder, flux, and tinning method, the solder was applied to the thermoelectric material sample at three different temperature conditions. The three temperatures selected were 50°F, 100°F, and 150°F over the initial

melting point of the solder. As most of the solder alloys tested were not of a true eutectic combination there was a considerable spread between the initial melting point and true liquidus which was covered by the temperature levels selected.

Two techniques of applying the solder at the three different temperature conditions using four different fluxes were chosen to evaluate the effectiveness of the solder and tinning combination.

The pretreatment of the as-received thermoelectric materials was:

Degrease one minute in hot perchloroethylene, ultrasonic clean for five minutes in perchloroethylene, vacuum dry for 16 hours at 100°C and 25 inches mercury, and store in a dessicator until used in the tinning operation.

The techniques used to apply the solder to the thermoelectric material surfaces were:

1. Dip Tinning - Dip in flux and then dip in solder with the solder temperature varied from 50, 100, and 150°F over the melting point of the solder.
2. Abrade Tinning - Abrade in flux on a 96% Silica ground glass plate and then abrade on a stainless steel dam submerged in solder in a stainless steel solder pot with the temperature varied from 50, 100, and 150°F over the melting point of the solder.

The fluxes used in this analysis were:

HCl (conc.)

50% HCl (conc.) + 50% Zn Cl₂ (sat.)

Divco #335

20.8 wt % Zn Cl₂ + 2.3 wt % NH₄ Cl + 76.9 wt % H₂O

These fluxes have been used with some success in the past work.

The solders investigated were:

<u>Solder</u>	<u>Melting Point</u>
45% Bi - 45% In - 10% Sn	170°F
50% Bi - 47.5% Sn - 2.5% Sb (BAT)	273°F
57% Bi - 43% Sn (Bi - Sn Eutectic)	282°F
70% Bi - 30% Sn	334°F
69% Bi - 29% Sn - 2% Sb	335°F *
79% Bi - 19% Sn - 2% Sb	390°F *
75% Sn - 24% Bi - 2% Sb	390°F *
74% Sn - 25.5% Bi - .5% Sb	390°F *
74% Sn - 21% Bi - 5% Sb	400°F *
95% Sn - 5% Bi	437°F
100% Bi	520°F

*NOTE: The melting point of these solders were determined with an iron-constantan thermocouple as the solder was melted in the solder pot.

After the thermoelectric elements were tinned they were potted in epoxy resin, cut so that the solder-element interface at the center section of the element was visible, polished, and inspected at 100X magnification to determine the quality of the interface.

Several of the solders investigated would not adhere to the surface of the thermoelectric elements at any of the three temperatures selected with any of the fluxes or by either tinning technique. The solders that demonstrated complete failure are:

45% Bi - 45% In - 10% Sn
57% Bi - 43% Sn
70% Bi - 30% Sn
95% Sn - 5% Bi
74% Sn - 25.5% Bi, - .5% Sb

Therefore, it was evident that the only solders that would adhere to the element surfaces were those Bi - Sn solders that contained 2% or more antimony or 100% bismuth used as a solder. The effect of antimony on soldering characteristics was confirmed by adding 2% antimony to the 70% Bi - 30% Sn solder, which previously had failed to adhere, now making the composition of the solder 69% Bi - 29% Sn - 2% Sb. The new composition solder would adhere to the element surfaces thus yielding proof that antimony was the constituent causing the solder to adhere. Various percent ranges of bismuth and tin with 2% and 5% antimony were checked all yielding successful results. The ranges included 79% to 21% bismuth and 74% to 19% tin.

With this knowledge workable solders can be made and used with a wide range of melting points.

In an attempt to correlate the quality of the solder - element interface a subjective rating system was devised which was based on the relative size and number of voids or inclusions at the solder-element interface.

Symbol	Rating	Description
Q-1	Excellent	Perfect soldering, no voids in solder or at interface
Q-2	Good	Very few small voids in either solder or at the interface but not both
Q-3	Fair	Few small voids in solder or at interface or mixture of very few small and very few medium voids at interface
Q-4	Poor	Many small and/or medium voids at interface and/or in solder
Q-5	Failure	Many large, small, and medium voids in solder and/or at the interface

In the Tables presented in Section IV, Data Summary, only the symbol representing the quality of joint will be used. Tinning refers to the process of applying solder to the thermoelectric element surfaces. In the subjective evaluation, one element of each type (n and p types), each having two solder-element interfaces, was chosen at random from three samples and inspected.

From the data presented, it can be seen that the quality of the element-solder interfaces obtained by the abrading technique is not as high as that obtained in dip tinning. This is probably due to the greater amount of debris and contaminants on the surface of the as-received element used in the abrading section of the analysis and not the fault of the technique, flux, or solder. The variation in condition of the elements received from the supplier appears to be a very significant variable and a variable that is difficult to control. This problem is being reviewed with the material manufacturer.

One possible means of controlling this variable to achieve a consistent, high integrity junction would be a standard pretreatment of the element surfaces prior to tinning but as was mentioned previously such a method has not been discovered to date.

During the solder analysis the effect of the flux seemed to be about the same regardless of the flux composition. Some fluxes were much easier to use than others due to the constituents of the flux and the temperature of the solder. In all cases, the 50% HCl + 50% Zn Cl_2 flux left heavy crystalline residues on the surface of the solder pot which inhibited the tinning operation and the cleanliness of the junction produced. HCl (conc.) was very difficult to use with high melting point solders due to its low flashing point. The reaction of HCl (conc.) in the high temperature solders was so violent in many cases that solder was splattered over the entire area of the sides of the element.

Generally Divco #335 flux had the most desirable characteristics for high melting point solders and was nearly as good for the low melting point solders as the other fluxes.

As a back check of the flux investigation, several polished samples were used in the tinning process, however they demonstrated success only when HCl (conc.) was used. A possible explanation of this phenomena could be that since HCl (conc.) was the only flux that etched the polished surface it would appear that the element surface must be roughened slightly before the solder will adhere to the element surface. Or, since the HCl (conc.) has a lower flashing point, the more violent reaction of HCl (conc.) as it flashes may be necessary to reduce the surface tension between the solder and the element surface to the point where the solder will adhere to the smooth element surface.

B. SURFACE ANALYSIS

In order to identify possible contaminants on the prepared thermoelectric material surfaces limited electron diffraction studies were conducted at the University of Michigan.

N type material samples were prepared by cutting the material to the required two millimeter length and then subjecting them to the cleaning process outlined in the Solder Analysis Section of this report. Three samples were then polished using gamal alumina, washed with distilled water and stored in a dessicator until examined.

The electron diffraction patterns produced for the three polished samples showed only Debye rings produced by aluminum oxide impacted in the surface by the polishing process. No bismuth-telluride rings appeared. The coverage of aluminum oxide was complete as traverses of the surface indicated identical diffraction patterns.

Two of the polished samples were treated at room temperature with Zinc Chloride - HCl flux and Ammonium Chloride - Zinc Chloride flux respectively and new diffraction patterns were produced. These patterns showed less intense Debye rings for aluminum oxide and the emergence of Debye rings for pure bismuth. This, indicates a positive cleaning action of the flux.

It is extremely difficult to differentiate between aluminum oxide and bismuth as both exhibit strong or intense Debye rings at approximately the same locations. Material identification in this case must be made using less intense rings which differ in spacing for the two materials.

As the electron beam penetration is a maximum of 100 angstroms below the surface, it is felt that this method of evaluation will lead to determination of a "clean" bismuth telluride surface.

The other method used for examination of the sample surface at this time involved production of collodion replicas. This method permits the examination of surface contour and also can be used for evaluation of bits of material stripped by removal of the replica from the sample.

Examination of several replicas taken from the polished samples showed small dark areas which could be material withdrawn from the surface. One transmission diffraction pattern showed slight evidence of aluminum oxide, however this was masked for the most part by evaporated palladium which was used to shadow the replica. Probably a heavier replica which can exert a greater stripping action will remove sufficient material for precise examination.

As an adjunct to the problem of determination of surface cleanliness, cathodic etching of samples was attempted. No real data has been generated as yet, however, the process has been made to work on bismuth telluride. The atmosphere supplying ions for bombardment of the bismuth telluride surface is argon at a pressure of approximately ten microns. The determination of the relationship between pressure, etch current, and etch time, to remove a predetermined amount of sample surface is now in process.

C. JUNCTION AGING STUDY

During the last quarter's work the resistance scanning apparatus was modified to increase its sensitivity from approximately 1×10^{-6} ohms to 1×10^{-7} ohms.

At the same time the probe apparatus was also modified to provide a more stable scan of the sample. The data taken prior to these modifications was not of sufficient reliability to insure the required accuracy of result and therefore will not be reported. Reruns of the resistance scans for the aging study samples are now in process and will be completed shortly.

III. PLAN FOR NEXT QUARTERLY PERIOD

- A. Work on cathodic etch process and evaluation using electron microscopy will continue.
- B. The bismuth - tin - antimony solder series will be examined more closely and the best combination of solder alloy, flux, and application method will be determined.
- C. Electropolishing will be evaluated as a cleaning technique.
- D. Mechanical testing of prepared samples will be initiated.
- E. Ultrasonic tinning of samples with bismuth - tin - antimony solder will be initiated.

IV. DATA SUMMARY

DATA SUMMARY - TABLE 1

Solder Method - Dip Tinning

Solder Alloy - 50% Bi - 47.5% Sn - 2.5% Sb

(P - type)

Flux	(MP + 50°F) 325°F	(MP + 100°F) 375°F	(MP + 150°F) 425°F
HCl (conc.)	Tins Fairly Easily Q-5	Tins Easily Q-3	Tins very easily Q-3
50 HCl + 50 Zn Cl ₂	Tins easily Q-4	Tins easily Q-4	Tins easily Q-3
NH ₄ Cl + Zn Cl ₂	Tins easily Q-4	Tins easily Q-3	Tins easily Q-2
Divco #335	Tins easily Q-5	Tins easily Q-3	Tins easily Q-2

(N - type)

Flux	MP + 50°F	MP + 100°F	MP + 150°F
HCl (conc.)	Hard to tin Q-5	Very hard to tin Q-3	Very hard to tin Q-1½
50 HCl + 50 Zn Cl ₂	Hard to tin Q-4	Hard to tin Q-2½	Hard to tin Q-3
NH ₄ Cl + Zn Cl ₂	Hard to tin Q-5	Hard to tin Q-2½	Hard to tin Q-1½
Divco #335	Hard to tin Q-3	Very hard to tin Q-1½	Very hard to tin Q-2½

DATA SUMMARY - TABLE 2

Solder Method - Dip Tinning

Solder Alloy - 100% Bismuth

(P-type)

Flux	(MP + 50°F) 520°F	(MP + 100°F) 620°F	(MP + 150°F) 670°F
HCl (conc.)	Can not tin	Can not tin	Can not tin
50 HCl + 50 Zn Cl ₂	Hard to tin Q-4	Tins Easily Q-4	Tins easily Q-4
NH ₄ Cl + Zn Cl ₂	Hard to tin Q-5	Tins Easily Q-4	Tins easily Q-4
Divco #335	Tins very easily Q-3	Tins very easily Q-3	Tins very easily Q-4

(N-type)

Flux	MP + 50°F	MP + 100°F	MP + 150°F
HCl (conc.)	Can not tin	Can not tin	Can not tin
50 HCl + 50 Zn Cl ₂	Hard to tin Q-3	Tins easily Q-2	Tins easily Q-1½
NH ₄ Cl + Zn Cl ₂	Hard to tin Q-5	Tins easily Q-2	Tins easily Q-1½
Divco #335	Tins very easily Q-2½	Tins very easily Q-2	Tins very easily Q-2

DATA SUMMARY - TABLE 3

Solder Method - Abrade Solder and Flux

Solder Alloy - 50% Bi - 47.5% Sn - 2.5% Sb

(P-type)

Flux	(MP + 50°F) 325°F	(MP + 100°F) 375°F	(MP + 150°F) 425°F
HCl (conc.)	Tins easily Q-3	Tins easily Q-4	Hard to tin Q-3
50 HCl + 50 Zn Cl ₂	Tins easily Q-4	Tins easily Q-4	Hard to tin Q-3
NH ₄ Cl + Zn Cl ₂	Hard to tin Q-3	Hard to tin Q-3	Hard to tin Q-3
Divco #335	Tins easily Q-4	Tins easily Q-2	Tins easily Q-1

(N-type)

Flux	MP + 50°F	MP + 100°F	MP + 150°C
HCl (conc.)	Tins easily Q-4	Tins easily Q-4	Hard to tin Q-3
50 HCl + 50 Zn Cl ₂	Tins easily Q-4	Tins easily Q-2	Hard to tin Q-2½
NH ₄ Cl + Zn Cl ₂	Tins easily Q-3	Hard to tin Q-4	Can not tin
Divco #335	Tins very easily Q-2	Tins easily Q-3	Tins easily Q-1½

DATA SUMMARY - TABLE 4

Solder Method - Abrade Solder and Flux

Solder Alloy - 74% Sn - 24% Bi - 2% Sb

(P-type)

Flux	(MP + 50°F) 440°F	(MP + 100°F) 490°F	(MP + 150°F) 540°F
HCl (conc.)	Hard to tin Q-5	Tins easily Q-5	Hard to tin Q-5
50 HCl + 50 Zn Cl ₂	Tins easily Q-4	Tins easily Q-5	Hard to tin Q-4
NH ₄ Cl + Zn Cl ₂	Tins easily Q-4	Hard to tin Q-3½	Can not tin
Divco #335	Tins easily Q-4	Hard to tin Q-5	Hard to tin Q-3½

(N-type)

Flux	MP + 50°F	MP + 100°F	MP + 150°F
HCl (conc.)	Hard to tin Q-3	Tins easily Q-4	Hard to tin Q-3
50 HCl + 50 Zn Cl ₂	Hard to tin Q-2½	Hard to tin Q-5	Hard to tin Q-5
NH ₄ Cl + Zn Cl ₂	Hard to tin Q-3	Can not tin	Can not tin
Divco #335	Easy to tin Q-4	Hard to tin Q-4	Hard to tin Q-4